

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : A61K 7/48	A1	(11) International Publication Number: WO 98/00105 (43) International Publication Date: 8 January 1998 (08.01.98)
<p>(21) International Application Number: PCT/EP97/03064</p> <p>(22) International Filing Date: 10 June 1997 (10.06.97)</p> <p>30) Priority Data: 60/020,745 28 June 1996 (28.06.96) US</p> <p>(71) Applicant (for AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SZ TT UG only): UNILEVER PLC (GB/GB); Unilever House, Blackfriars, London EC4P 4BQ (GB).</p> <p>(71) Applicant (for all designated States except AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SZ TT UG): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).</p> <p>(72) Inventors: DOBKOWSKI, Brian, John; 31 Wakeley Street, Shelton, CT 06484 (US). ZNAIDEN, Alexander, Paul; 110 Fox Road, Trumbull, CT 06611 (US). CHENEY, Michael, Charles; 383 Sigwin Drive, Fairfield, CT 06430 (US). ROSE, Walter; 95 Roydon Road, New Haven, CT 06511 (US).</p> <p>(74) Agent: ROTS, Maria, Johanna, Francisca; Unilever PLC, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: COSMETIC COMPOSITIONS CONTAINING A SILOXANE ELASTOMER</p> <p>(57) Abstract</p> <p>A skin treatment composition is provided which includes a crosslinked non-emulsifying siloxane elastomer, a skin conditioning agent, a volatile siloxane and no more than 5 % water. Hydrocarbons such as petrolatum and polyols such as glycerin are the preferred skin conditioning agents. Inclusion of the elastomer provides a non-traditional smooth/silky feel to the skin upon application with a non-draggy rub in.</p>		

- 1 -

COSMETIC COMPOSITIONS CONTAINING A SILOXANE ELASTOMER

5 BACKGROUND OF THE INVENTIONField of the Invention

10 The invention relates to anhydrous cosmetic compositions for topical application to the skin whose properties are enhanced by incorporation of certain elastomeric silicones.

15 The Related Art

Emollients including organic esters and hydrocarbons, especially petrolatum, have long been used medicinally as skin conditioning agents. These substances are second
20 only to water as moisturizing ingredients of choice. They function primarily as an occlusive barrier. The water content of the outer layers of human skin stratum corneum is a controlling factor in the appearance of dry skin symptoms. When the stratum corneum contains an adequate
25 amount of water within the range of ten to twenty percent, the skin remains flexible. However, when the water content falls below ten percent the stratum corneum often becomes brittle and rough and can exhibit scaling and cracking.

30 The stratum corneum receives its water from the deep layers of the epidermis by diffusion or when it is brought into direct contact with water. The diffusion process is controlled by the water content of the skin as well as the
35 concentration gradient. In a very dry environment, the water loss from the external skin layers can be

- 2 -

significant and often exceeds the rate of replacement by diffusion. An occlusive or semi-occlusive barrier substance placed on the surface of the skin acts to retard water loss to the environment. It also allows the skin surface to rehydrate via a diffusion mechanism.

While there are many effective and economical skin conditioning agents, they nevertheless suffer from certain disadvantages.

Often the emollient types are delivered as water in oil emulsions. It is difficult to attain the critical formula balance between oil and water phases to an extent sufficient to ensure long term storage stability. One part of this critical balance is the internal phase volume. A critical volume must be obtained to maximize the chemical and physical interactions which produce and stabilize the system. If this critical volume is not balanced properly the product may suffer from viscosity change and eventual phase separation. Usually the optimum volume is quite large which limits the external phase volume size, and gives the system a draggy unfavorable slow break attribute. This critical internal phase volume restriction can reduce functionality and add unfavorable feel characteristics.

Anhydrous systems avoid emulsion stability problems. Unfortunately other aesthetic issues arise with anhydrous systems. Not all oily phase materials are compatible at high concentration. Moreover, occlusive agents such as petrolatum are relatively greasy. They suffer the disadvantage of transfer onto clothing and are not easily removed from the skin by washing with soap. Neither do they allow for adequate penetration into the epidermis.

- 3 -

U.S. Patent 5,387,417 (Rentsch) reports obtaining cosmetically acceptable, translucent moisturizing lotions through emulsification of a petrolatum base with a crosslinked organopolysiloxane-polyoxyalkylene emulsifier.

5 According to the disclosure, not only is compatibility achieved but this siloxane allows for matching of refractive indices for the continuous and discontinuous phases.

10 U.S. Patent 5,280,019 (Klimisch) reports compositions which enhance the absorption and retention of moisturizer on the skin. These results are achieved through use of an organosilicon compound which is a carboxy functionalized polysiloxane or its metal carboxylate salt.

15 Evident from the foregoing art is that certain types of polysiloxanes incorporating hydrophilic functionality, e.g. polyoxyalkylene or carboxylate units, can assist in the emulsification of oily phases. Indeed these
20 disclosures suggest the requirement for hydrophilic functionality on the silicones. Incorporation of hydrophilic groups for emulsification unfortunately detracts from the ability of silicones to provide a soft, silky afterfeel. These prior art hydrophilic silicones
25 also do not fully solve oil and water phase compatibility problems. New systems are needed to carry relatively high levels of aqueous based moisturizing ingredients (e.g. glycerin). Also necessary are silicones that can achieve a smoother emulsion break to maximize positive
30 sensory/feel attributes when the emulsions are rubbed into the skin. Anhydrous systems of occlusives are also not benefitted from hydrophilic bearing silicones which often lead to phase separation.

35

system and deliver an unusually soft, silky afterfeel to skin.

5 Crosslinked non-emulsifying siloxane elastomers are the first essential element of this invention. They will usually have an average number molecular weight in excess of 2,000, preferably in excess of 1,000,000. Typically they will range from 10,000 to 20 million. The term "non-emulsifying" defines a siloxane from which polyoxyalkylene units are absent. Advantageously the elastomers are 10 formed from a divinyl compound, particularly a polymer with at least two free vinyl groups, reacting with Si-H linkages of a polysiloxane backbone such as a molecularly spherical MQ resin. Suitable elastomer compositions are commercially available from the General Electric Company 15 under product designation General Electric Silicone 1229 with proposed CTFA name of Cyclomethicone and Vinyl Dimethicone/Methicone Cross Polymer, delivered as 20-35% elastomer in a cyclomethicone carrier. A related 20 elastomer composition under the CTFA name of Crosslinked Stearyl Methyl Dimethyl Siloxane Copolymer is available as Gransil SR-CYC (25-35% elastomer in cyclomethicone) from Grant Industries, Inc., Elmwood Park, New Jersey. The commercial products from General Electric and Grant 25 Industries preferably are further processed by subjecting them to a high pressure (approximately 5,000 psi) treatment in a Sonolator with recycling in 10 to 60 passes. Sonolation achieves a resultant fluid with elastomer average particle size ranging from 0.2 to 10 30 micron, preferably 0.5 to 5 micron. Viscosity is best when ranging between 300 and 20,000 cps at 25°C as measured by a Brookfield LV Viscometer (size 4 bar, 60 rpm, 15 sec.).

- 7 -

Amounts of the elastomer may range from 0.1 to 30%, optimally from 1 to 15%, most preferably from 3 to 10% by weight of the composition.

- 5 A second essential element of the present invention is that of a skin conditioning agent. These agents preferably are selected from humectants, exfoliants, emollients, and mixtures thereof.
- 10 Humectants usually are polyhydric alcohols intended for moisturizing, reducing scaling and stimulating removal of built-up scale from the skin. Typical polyhydric alcohols include polyalkylene glycols and more preferably alkylene polyols and their derivatives. Illustrative are propylene
- 15 glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol, sorbitol, hydroxypropyl sorbitol, hexylene glycol, 1,3-butylene glycol, 1,2,6-hexanetriol, ethoxylated glycerin, propoxylated glycerin and mixtures thereof. Most preferably the humectant is glycerin.
- 20 Amounts of humectant may range anywhere from 1 to 50%, preferably from 10 to 40%, optimally from 25 to 35% by weight.
- Exfoliants according to the present invention are
- 25 preferably selected from alpha-hydroxycarboxylic acids, beta-hydroxycarboxylic acids and salts of these acids. The carboxylic acids preferably are C₂-C₃₀ carboxylic acids. Most preferred are glycolic, lactic and salicylic acids and their ammonium salts. Amounts of the exfoliants
- 30 preferably range from 1 to 15%, more preferably from 2 to 10% by weight.

- 8 -

A wide variety of C₂-C₃₀ alpha-hydroxycarboxylic acids may be employed. Suitable examples of which include:

- 5 -hydroxyethanoic acid
- hydroxypropanoic acid
- hydroxyhexanoic acid
- hydroxyoctanoic acid
- hydroxydecanoic acid
- hydroxydodecanoic acid
- 10 -hydroxytetradecanoic acid
- hydroxyhexadecanoic acid
- hydroxyoctadecanoic acid
- hydroxyeicosanoic acid
- hydroxydocosanoic acid
- 15 -hydroxyhexacosanoic acid, and
- hydroxyoctacosanoic acid

When the conditioning agent is an emollient it is preferably be selected from hydrocarbons, fatty acids, fatty alcohols and esters. Petrolatum is the most preferred hydrocarbon type of emollient conditioning agent. Other hydrocarbons that may be employed include mineral oil, polyolefins such as polydecene, and parafins such as isohexadecane (e.g. Permethyl 99® and Permethyl 101®).

Fatty acids and alcohols preferably have from 10 to 30 carbon atoms. Illustrative of this category are pelargonic, lauric, myristic, palmitic, stearic, isostearic, hydroxystearic, oleic, linoleic, ricinoleic, arachidic, behenic and erucic acids and alcohols.

Oily ester emollients preferably are those selected from one or more of the following classes:

1. Triglyceride esters such as vegetable and animal fats and oils. Examples include castor oil, cocoa butter, safflower oil, cottonseed oil, corn oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil, sesame oil, squalene, Kikui oil and soybean oil.
2. Acetoglyceride esters, such as acetylated monoglycerides.
3. Ethoxylated glycerides, such as ethoxylated glyceryl monostearate.
4. Alkyl esters of fatty acids having 10 to 20 carbon atoms. Methyl, isopropyl, and butyl esters of fatty acids are useful herein. Examples include hexyl laurate, isohexyl laurate, isohexyl palmitate, isopropyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, diisopropyl adipate, diisohexyl adipate, dihexyldecyl adipate, diisopropyl sebacate, lauryl lactate, myristyl lactate, and cetyl lactate.
5. Alkenyl esters of fatty acids having 10 to 20 carbon atoms. Examples thereof include oleyl myristate, oleyl stearate, and oleyl oleate.
6. Ether-esters such as fatty acid esters of ethoxylated fatty alcohols.
7. Polyhydric alcohol esters. Ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol (200-6000) mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol 2000 monooleate, polypropylene glycol 2000 monostearate, ethoxylated propylene glycol

- 10 -

monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol polyfatty esters, ethoxylated glyceryl monostearate, 1,2-butylene glycol monostearate, 1,2-butylene glycol distearate, 5 polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters are satisfactory polyhydric alcohol esters.

10 8. Wax esters such as beeswax, spermaceti, myristyl myristate, stearyl stearate.

Amounts of the skin conditioning agent may range from 1 to 50%, preferably from 3 to 25%, optimally from 5 to 20% 15 by weight.

A third essential element of the present invention is that of a volatile siloxane. The term "volatile" refers to those materials having a measurable pressure at ambient 20 conditions. Volatile polyorganosiloxanes useful herein may be cyclic or linear. Preferred cyclic silicones include polydimethylsiloxanes containing from about 3 to about 9 silicon atoms, preferably containing from about 4 to about 5 silicon atoms, generally known as 25 cyclomethicones. Preferred linear silicone oils include the polydimethylsiloxanes containing from about 3 to about 9 silicon atoms. The linear volatile silicones generally have viscosities of less than about 5 centistokes at 25°C, while the cyclic materials have viscosities of less than 30 about 10 centistokes, the preferable range being from 0.1 to 8 centistokes. Examples of silicone oils useful in the present invention include: Dow Corning 244, Dow Corning 245, Dow Corning 344, Dow Corning 345 and Dow Corning 200 (manufactured by the Dow Corning Corporation); Silicone 35 7207 and Silicone 7158 (manufactured by the Union Carbide Corporation); SF1202 (manufactured by General Electric).

- 11 -

Amounts of the volatile siloxane will range from 10 to 80%, preferably from 20 to 70%, optimally from 30 to 65% by weight.

5 Cosmetic compositions of the present invention are essentially anhydrous. The amount of water will be confined to range from 0 to 5%, preferably not above 4%, more preferably not above 3%, most preferably not above 2% optimally not above 0.5% by weight.

10 Beyond the basic components, other materials may be included depending upon the particular type of cosmetic composition sought. For instance, surfactants may be formulated into the compositions. These may be selected
15 from nonionic, anionic, cationic or amphoteric emulsifying agents. They may range in amount anywhere from about 0.1 to about 20% by weight. Illustrative nonionic surfactants are alkoxyated compounds based on C₁₀-C₂₂ fatty alcohols and acids, and sorbitan. These materials are available,
20 for instance, from the Shell Chemical Company under the Neodol trademark. Copolymers of polyoxypropylene-polyoxyethylene, sold by the BASF Corporation under the Pluronic trademark, are sometimes also useful. Alkyl polyglycosides available from the Henkel Corporation may
25 also be utilized for purposes of this invention.

30 Anionic type surfactants include fatty acid soaps, sodium lauryl sulphate, sodium lauryl ether sulphate, alkyl benzene sulphonate, mono- and di-alkyl acid phosphates and sodium fatty acyl isethionate.

35 Amphoteric surfactants include such materials as dialkylamine oxide and various types of betaines (such as cocoamidopropyl betaine).

- 12 -

Minor adjunct ingredients may also be included such as fragrances, opacifiers and colorants, each in their effective amounts to accomplish their respective functions.

The following examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

EXAMPLE 1

This Example illustrates an anhydrous skin treatment composition. Components listed in the Table below were added together in a vessel at 60°C and mixed with a homogenizing agitator. Thereafter they were subjected to sonolation at 800-1,000 psi for five to ten minutes. The resultant product was a non-greasy semi-solid with a very silky afterfeel.

TABLE I

COMPONENT	WEIGHT %
Petrolatum	18.5
Gransil SR-CYC	30
DC 344 Fluid7	51.5

EXAMPLE 2

This Example illustrates another anhydrous skin treatment composition according to the present invention. The

- 13 -

formulation was prepared in a manner essentially similar to that of Example 1 utilizing the components listed in the Table below. The resultant product had a smooth, silky afterfeel.

5

TABLE II

10

COMPONENT	WEIGHT %
Petrolatum	22
Gransil SR-CYC	43
DC 244 Fluid7	35

15

EXAMPLE 3

20

A series of experiments were performed to evaluate the effect of water upon compositions of the present invention. Formulations and performance characteristics are listed under Table III.

TABLE III

COMPONENTS	CTFA NOMENCLATURE	FORMULATION (WEIGHT %)			
		A	B	C	D
GE SE1229 (25% elastomer in D4/D5 volatile silicone)	Vinyldimethicone/ Methicone Crosspolymer	31	31	31	31
Dow 345 Silicone fluid	Cyclomethicone	31	38	35	26
Dow 344 silicone fluid	Cyclomethicone	8.5	8.5	8.5	8.5
Petroleum Jelly	Petrolatum	11	11	11	11
Glycerin (DRY)	Glycerin	8	8	8	8
Abil EM90	Cetyl Dimethicone Copolyol	0.5	0.5	0.5	0.5
DI Water	Deminerlized Water	0	3	6	15
PERFORMANCE:					
Initial Feel Upon Application To Skin		BEST	GOOD	NOT GOOD	NOT GOOD
		non traditional smooth/silky "powdery" application non draggy upon rub in	non traditional smooth/silky "powdery" application slightly draggy upon rub in	more traditional losing "powdery" transition to upon application to draggy upon rub in	traditional rub in transition upon application very draggy upon rub in
Phase Stability (Freeze/Thaw)		Pass	Pass	Fail	Fail

- 15 -

Results of the experiments in Table III indicate that formulations containing 6% water fail in the freeze/thaw cycling stability evaluation. Moreover, the skinfeel of the product upon initial application demonstrates that at 6% water, there is a draggy sensation upon rub in. By contrast, at 0% water a smooth rub in was observed. When 3% water was present, there was only a slightly draggy feel.

10

CLAIMS

- 5 1. A skin treatment composition comprising:
- (i) from 0.1 to 30% of a crosslinked non-
- emulsifying siloxane elastomer;
- 10 (ii) from 1 to 50% of a skin conditioning agent;
- (iii) from 10 to 80% of a volatile siloxane; and
- (iv) from 0 to 5% of water.
- 15 2. A composition according to claim 1 wherein the skin
- conditioning agent is selected from the group
- consisting of humectants, exfoliants, emollients and
- mixtures thereof.
- 20 3. A composition according to claim 2 wherein the
- emollient is a hydrocarbon.
- 25 4. A composition according to claim 3 wherein the
- hydrocarbon is petrolatum.
- 30 5. A composition according to any one of claims 2-4
- wherein the humectant is a polyol selected from the
- group consisting of glycerin, propylene glycol,
- polyethylene glycol and mixtures thereof.
- 35 6. A composition according to any one of claims 2-5
- wherein the exfoliant is selected from the group
- consisting of alpha-hydroxycarboxylic acid,
- beta-hydroxycarboxylic acid and salts thereof.
7. A composition according to any one of claims 1-6

- 17 -

wherein water is present from 0 to 3% by weight.

- 5 8. A composition according to any one of claims 1-7 wherein the crosslinked non-emulsifying siloxane elastomer is formed from a divinyl compound reacting with Si-H linkages of a polysiloxane.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/03064

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 0 790 055 A (OREAL) 20 August 1997 see the whole document	1-3,7,8
X	EP 0 295 886 A (TORAY SILICONE CO) 21 December 1988 see the whole document	1-3,5,7, 8
X	CHEMICAL ABSTRACTS, vol. 124, no. 4, 22 January 1996 Columbus, Ohio, US; abstract no. 37399, TAKAHASHI, HIDEKI ET AL: "Two-layer oily makeup cosmetics containing spherical powders of organopolysiloxane elastomers and hydrophobic-treated powders" XP002044866 see abstract & JP 07 267 820 A (SHISEIDO CO LTD, JAPAN)	1-3,7

-/--

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "A" document member of the same patent family

Date of the actual completion of the international search

28 October 1997

Date of mailing of the international search report

11. 11. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3018

Authorized officer

Sierra Gonzalez, M

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP 97/03064

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	CHEMICAL ABSTRACTS, vol. 126, no. 8, 24 February 1997 Columbus, Ohio, US; abstract no. 108665, KURODA, AKIHIRO: "Makeup cosmetics containing fine powders and fluoroalkyl-modified silicates" XP002044867 see abstract & JP 08 301 727 A (KANEBO LTD, JAPAN)	1-3,7
P,X	--- CHEMICAL ABSTRACTS, vol. 126, no. 8, 24 February 1997 Columbus, Ohio, US; abstract no. 108664, KURODA, AKIHIRO ET AL: "Sunscreens containing metal oxides, polyoxyalkylene-polysiloxanes, and elastomers or resin waxes" XP002044868 see abstract & JP 08 295 620 A (KANEBO LTD, JAPAN)	1-3,7,8
A	--- CHEMICAL ABSTRACTS, vol. 127, Columbus, Ohio, US; abstract no. 166546, YANAGIDA, TAKESHI ET AL: "Makeups containing powders of silicone rubber and water-absorbing polymer" XP002044869 see abstract & JP 09 175 939 A (SHISEIDO CO., LTD., JAPAN) -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP 97/03064

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0790055 A	20-08-97	FR 2744911 A	22-08-97

EP 0295886 A	21-12-88	JP 4066446 B	23-10-92
		JP 63313710 A	21-12-88
		CA 1319306 A	22-06-93
		DE 3867329 A	13-02-92
